UNSYMMETRICAL FLUORINE-CONTAINING DISULFIDES

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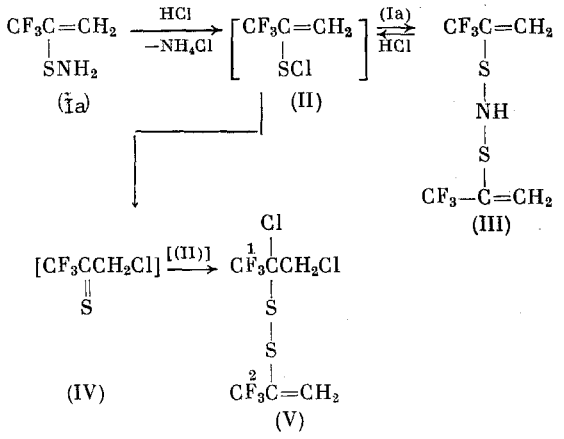
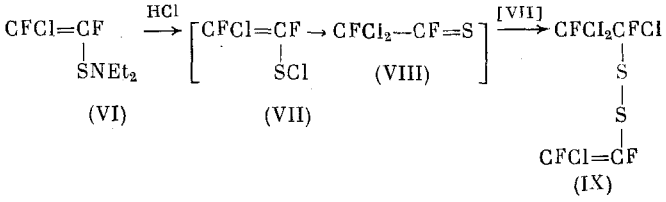
One of the main methods for the synthesis of unsymmetrical disulfides [1, 2] involves nucleophilic displacement reactions on the S atom of sulfenyl derivatives upon treatment with thiols and thiolate anions [3-5]. In the present paper we describe the synthesis of unsymmetrical fluorine-containing disulfides, which have not previously been available.

Reaction of the α,β-unsaturated sulfenamide (Ia) with dry HCl in ether or CH_2Cl_2 leads to the formation of the disulfide (V):



It is known that saturated sulfenamides react with HCl to generate sulfenyl chlorides (SFC) [6]; it is assumed, therefore, that (Ia) reacts with HCl to give an α,β-unsaturated SFC (II), which is converted in the presence of the sulfenamide starting material (Ia) to the bis(alkenylthio)amine (III),† which is the final reaction product in the presence of a limiting amount of HCl. In the presence of excess HCl, (III) is cleaved back to the SFC (II), which isomerizes to the thioketone (IV) under the reaction conditions (cf. [8]); the latter then undergoes an addition reaction at its thiocarbonyl group with the SFC (II) to generate the disulfide (V).

The disulfide (VI) is obtained in an analogous manner upon treatment of 1,2-difluoro-2-chlorovinyl-N,N-diethylsulfenamide (VI) with HCl in CH_2Cl_2 or $CHCl_3$‡:



*Deceased.

†Bis- and tris(alkylthio)amines are obtained as the reaction products of SFC with NH_3 or primary amines [6, 7].

‡This reaction product has previously been erroneously described as CFCl=CF–S–CF(SCl)$CFCl_2$ [8]. The mass spectrum is consistent with structure (IX): intense peaks at m/e 167 [$CFCl_2$ $CFCl]^+$ and 161 [$CFClClFS_2]^+$ are seen. ^{19}F NMR and IR spectroscopy do not allow one to distinguish between the two structural possibilities, viz., [IX] and CFCl=CFSCF(SCl)$CFCl_2$.

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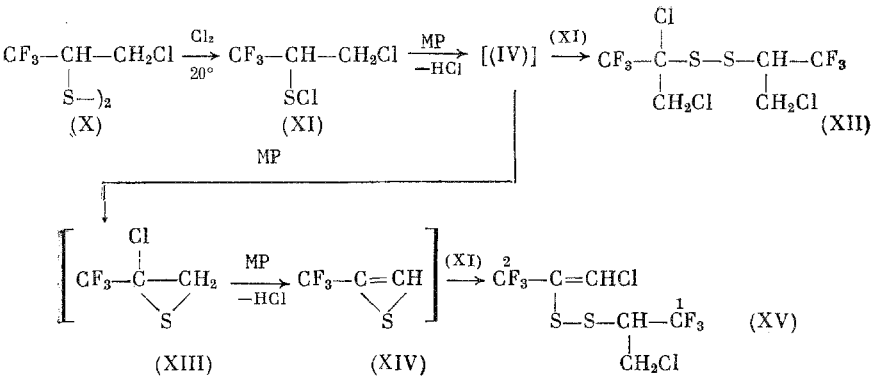
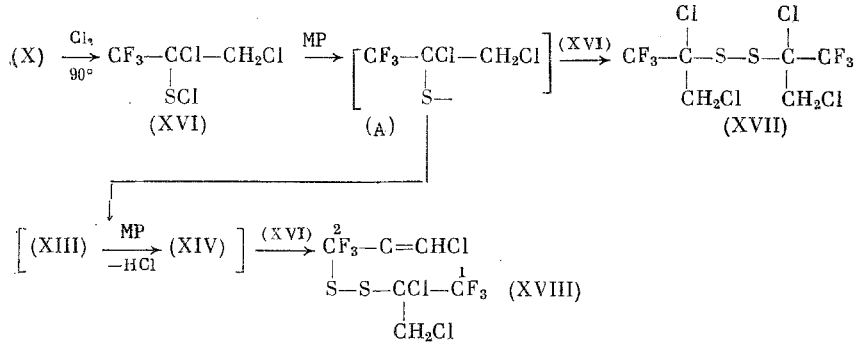
A mixture of disulfides (XII) and (XV) in a 73:27 ratio was obtained upon reaction of N-methylpyrrolidone (MP) with SFC (XI), which has been reported previously as the chlorination cleavage product of the disulfide (X):



Dehydrochlorination of the SFC (XI) is assumed to lead to the α-chlorothioketone (IV), which can react along two pathways: addition of starting material (XI) to the thiocarbonyl group to give the disulfide (XII), or isomerization to the thioepoxide (XIII) in the presence of MP, followed by dehydrochlorination* and ring opening of the resulting thiirene (XIV)† upon interaction with the SFC starting material (XI) to give the disulfide (XV).

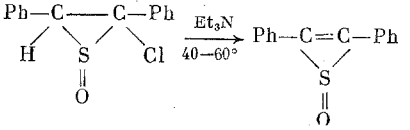
Reaction of MP with the α,β-dichloro SFC (XVI) [prepared via chlorination of disulfide (X) or SFC (XI) at 90°] gives a mixture of the disulfides (XVII) and (XVIII) in a 73:27 ratio:

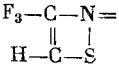


This conversion may be regarded as involving preliminary halophilic reaction [12] to give the mercaptide (A) [12]. This compound can then react with the SFC starting material (XVI) in a nucleophilic displacement sequence to generate the disulfide (XVII),‡ or, alternatively, it can undergo elimination of chloride from the β position, which is favorable due to intramolecular stabilization of the mercaptide A. The resulting thioepoxide (XIII) can generate thiirene (XIV) according to the sequence described above; cleavage of the latter with the SFC starting material (XVI) would give the disulfide (XVIII).

One of the most important steps in the reactions discussed above apparently involves formation of thiocarbonyl compounds and addition reactions of these compounds at their thio-

*2,3-Diphenylthiirene-1-oxide was obtained via the following reaction [10]:



†The formation of trifluoromethylthiirene (XIV) upon photolysis of  has been reported previously [11].

‡The formation of disulfides upon treatment of fluorine-containing α,β-unsaturated SFC with MP has also been reported previously [8].

TABLE 1

$CF_3C(SR)=C(H^1)(H^2)$

Compound	R	^{19}F NMR spectrum, CF_3, ppm	PMR spectrum (δ, ppm, J, Hz)			IR spectrum νC=C, cm^{-1}
			H^1	H^2	R	
(Ia)	NH_2	−13.2 s	5,87 br.s.	5,55 br.s.	2.72 br.s.(NH_2)	1620
(Ib)	$N(C_2H_5)_2$	−13,1 s	5,87 br.s.	5,67 br.s.	3.05 q (CH_2), 1.15 t (CH_3) *	1620
(XIX)	PhCO	−10,2s	5,9 s	6,5 s	7,4m (C_6H_5)	1630

*$J_{CH_2-CH_3}$ = 8 Hz.

TABLE 2

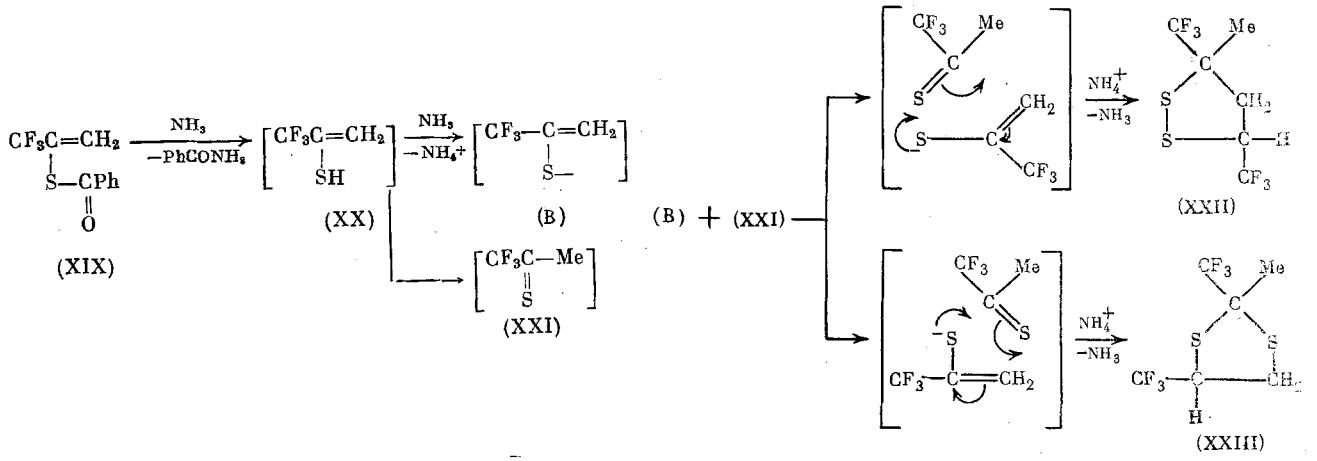
$CF_3CH(SR)-CH_2Cl$

Compound	R	^{19}F NMR spectrum (δ, ppm, J, Hz)		PMR spectrum (δ, ppm)		
		CF_3	J_{CF_3-CH}	CH_2Cl	CH	R
(XXV)	PhCO	−10,2 d	7,5	3,6 m	4,6 m	7,4m (C_6H_5)
(XXVIa)	NH_2	−9,55 d	9,4	4,02 m	3,36 m	2,87 (NH_2)
(XXVIb)	$N(C_2H_5)_2$	−10,0 d	8,5	4,05 m	3,62 m	3,47 q (CH_2), 1,41 t (CH_3) *

*$J_{CH_2-CH_3}$ = 7 Hz.

carbonyl groups with sulfenyl chlorides according to a conventional polarization, $-\overset{\delta+}{S}-\overset{\delta-}{Cl}$ and $\overset{\delta+}{C}=\overset{\delta-}{S}$.

It is known that the polarization of the C=S group in fluorine-containing thioketones is not constant, and that nucleophilic attack can occur at the S atom as well as at the C atom [13]. This twofold reactivity profile was evident in our attempts to prepare the enethiol (XX) via cleavage of 1-trifluoromethylvinylthiobenzoate (XIX) upon treatment with NH_3. A mixture of cyclodimers of thioketone (XXI) was obtained, namely, the cyclic disulfide (XXIII) and 1,3-dithiolane (XXIII):



Nucleophilic cleavage of thioacid esters is an important method for the preparation of thiols [14]. The enethiol (XX) apparently isomerizes during the course of the reaction to the thioketone (XXI), which reacts further with thioenolate B (the reaction is carried out in the presence of excess NH_3) to generate compounds (XXII) and (XXIII). We have previously described the isomerization of fluorine-containing enethiols to thioketones under basic conditions and the subsequent formation of linear adducts of the enethiol and the thiocarbonyl group of the thioketone [15].

1-Trifluoromethylvinylthiobenzoate (XIX) was synthesized from SFC (XI) by sequential workup with H_2S [9], PhCOCl, and Et_3N:

$$(XI) \xrightarrow{H_2S} \underset{\underset{SH}{|}}{CF_3CHCH_2Cl} \xrightarrow[-HCl]{PhCOCl} \underset{\underset{S-CPh}{|}\\ \underset{O}{\|}}{CF_3CHCH_2Cl} \xrightarrow[-HCl]{Et_3N} (XIX)$$

(XXIV) (XXV)

The α,β-unsaturated sulfenamides (Ia and b) were obtained according to [8]:

$$(XI) \xrightarrow[-78°]{R_2NH} \underset{\underset{SNR_2}{|}}{CF_3CHCH_2Cl} \xrightarrow[-HCl]{B} \underset{\underset{SNR_2}{|}}{CF_3C=CH_2}$$

(XXVI a, b) (I a, b)

R = H (a), Et (b); B = KOH or Et_2NH.

Compounds (Ia and b) are unstable in the liquid state and decompose after several hours to give an undistillable mixture of products.

EXPERIMENTAL

^{19}F and ^1H NMR spectra were obtained on a Perkin-ELmer R-32B spectrometer (at 84.6 and 90 MHz, respectively), using CF_3CO_2H (^{19}F) and TMS (^1H) as internal standards. IR spectra were recorded on a UR-20 spectrophotometer. The purity of the compounds under investigation was monitored by GLC on an LKhM-8MD chromatograph (model 3) using a column coated with 20% QF on Chromaton. Preparative GLC of compounds (XII) and (XV) was carried out on a Fractovap GK-221 (Carlo Erba) chromatograph using a 4 m × 25 mm column filled with 20% QF on Chromaton at a column temperature of 160°C; compounds (XVII) and (XVIII) were purified on a Perkin-Elmer F-21 apparatus using a 5 m × 20 mm column of 20% QF-20 on Chromaton and a column temperature of 190°C. Mass spectra were recorded on a Varian MAT CH-8 spectrometer (at 70 eV); the m/e values reported are for the ^{35}Cl and ^{32}S isotopes and include the probable assignments. ^{19}F and ^1H NMR spectra of dithiolanes (XXII) and (XXIII) were obtained on a Bruker WP-200SY spectrometer (at 188.3 and 200.1 MHz, respectively) versus CF_3CO_2H as external standard (^{19}F) or TMS as internal standard (^1H, δ scale). ^{19}F and ^1H NMR and IR spectra of compounds (Ia and b) and (XIX) are presented in Table 1, those of compounds (XXV) and (XXVI a and b) in Table 2.

1,1,1-Trifluoro-2-propene-2-sulfenamide (Ia). A solution of 5.5 ml of absolute Et_2NH in 5 ml of absolute ether was cooled to −20°C, and a solution of 9.5 g of (XXVIa) in 5 ml of absolute ether was added slowly with stirring. The mixture was warmed to ∿20°C. Distillation of the filtrate yielded 3.2 g (42.3%) of (Ia), bp 30-35°C (18 mm). Found: C 25.86; H 2.87; F 39.24%. $C_3H_4F_3NS$. Calculated: C 25.17; H 2.28; F 39.82%.

1,1,1-Trifluoro-2-propene-N,N-diethyl-2-sulfenamide (Ib). Compound (XXVIb) (3.4 g) was distilled in vacuo (111 mm) over excess solid KOH. Yield 2.3 g (79.6%) of (Ib), bp 80°C (65 mm). Found: C 42.34; H 6.17; F 28.60%. $C_7H_{12}F_3NS$. Calculated: C 42.19; H 6.07; F 28.61%.

Bis(1,1,1-trifluoro-2-propene-2-mercapto)amine (III). A solution of 10 ml of absolute CH_2Cl_2 saturated with HCl was cooled to −20°C and 2.24 g of (Ia) was added. Distillation of the filtrate gave 1 g (47.6%) of (III), bp 36-38°C (1 mm). Found: C 26.57; ;H 1.83; F 42.42; S 23.79; N 5.20%. $C_6H_5F_6S_2N$. Calculated: C 26.77; H 1.87; F 42.34; S 23.82; N 5.20%. IR spectrum (ν, cm^{-1}): 1620 (C=C), 3400 br (NH). ^{19}F NMR spectrum: −12.4 s (CF_3). PMR spectrum: 4.06 br. s (NH), 5.56 br. s (H^1, $H^{1'}$), 5.83 br. s (H^2, $H^{2'}$), intensity ratio 1:2:2.

1-Trifluoromethylvinyl 1'-Trifluoromethyl-1',2'-dichloroethyl) Disulfide (V). a) A saturated solution of HCl in 15 ml of absolute ether was treated with 3.2 g of (Ia) at −20°C with periodic stirring. Distillation of the filtrate yielded 2.07 g (57.2%) of (V), bp 50-52°C (1 mm). Found: C 22.83; H 1.30; F 34.08; S 19.81%. $C_6H_4F_6Cl_2S_2$. Calculated: C 22.16; H 1.24; F 35.06; S 19.72%. Mass spectrum, m/e: 324 M^+, $^{194}[CF_3C_2H_2ClS_2]^+$, 165 $[CF_3C_2H_2Cl_2]^+$, 159 $[CF_3C_2H_2S_2]^+$, 140 $[CF_3C_2H_2S_2]^+$, 121 $[CFC_2H^2S^2]^+$, 69 $[CF_3]^+$. IR spectrum (ν, cm^{-1}): 1625 (C=C). ^{19}F NMR spectrum: −5.55 s (CF_3^1), −12.9 s (CF_3). PMR spectrum: 4.37 s (CH_2Cl), 6.5 m (H^1, H^2).

b) A solution of 2.0 g of (III) in 10 ml of absolute CH_2Cl_2 was charged with dry HCl while maintaining the temperature at 20-25°C; the extent of reaction was monitored by GLC.

Distillation of the filtrate gave 1.4 g (58.3%) of (V).

c) A solution of 2.2 g (Ia) in 10 ml of absolute CH_2Cl_2 was charged with dry HCl while maintaining the temperature at 20-25°C; the end of the reaction was followed by GLC. Distillation of the filtrate yielded 1.5 g (60%) of (V).

1,2-Difluoro-2-chlorovinyl 1'2'-Difluoro-1',2'2'-trichloroethyl Disulfide (IX). A solution of 3.8 g of 1,2-difluoro-2-chlorovinyl-N,N-diethylsulfenamide [8] in 20 ml of absolute CH_2Cl_2 was cooled to −20°C and purged with dry HCl; the extent of reaction was monitored by GLC. Distillation of the filtrate gave 1.6 g (43%) of a mixture of the cis and trans isomers of (IX) in a 62.38 ratio, bp 60°C (0.5 mm). IR spectrum (ν, cm^{-1}): 1650 (C=C). Mass spectrum, m/e: 328 M^+, 293 $[M-Cl]^+$, 227 $[M-CFCl_2]^+$, 167 $[CFClCFCl_2]^+$, 161 $[C_2F_2ClS_2]^+$, 129 $C_2F_2ClS]^+$, 101 $[CFCl_2]^+$. $CC\overset{1}{l}F=\overset{2}{C}F-\overset{3}{S}-\overset{4}{S}-CFCl-CFCl_2$. ^{19}F NMR spectrum: cis isomer: 2.5 d (F^1) 37.3 d.m (F^2), 11.8 d.m (F^3), −14.9 d.m (F^4), $J_{F^1-F^2}$ = 20.7, $J_{F^3-F^2}$ = 7.5, $J_{F^3-F^4}$ = 18.8, $J_{F^4-F^2}$ = 1.9 Hz; trans isomer: 19.3 d.m (F^1), 49.0 d.m (F^2), 1.23 d.d.d (F^3), −14.7 d.d (F^4), $J_{F^1-F^2}$ = 131.5 $J_{F^3-F^2}$ = 7.5, $J_{F^3-F^4}$ = 18.8, $J_{F^3-F^1}$ = 5.6 $J_{F^4-F^2}$ = 1.9 Hz.

Reaction of 1,1,1-Trifluoro-3-chloropropane-2-sulfenyl Chloride (XI) with N-Methylpyrrolidone. N-Methylpyrrolidone (20 ml) was cooled to −40°C and 8.3 g of (IX) was added dropwise with periodic agitation [9]. The mixture was maintained at −40°C for 1 h, then slowly warmed to ∿20°C; water was added, and the organic layer was dried over $MgSO_4$ and distilled. Yield 5.3 g of a mixture, bp 53-75°C (1 mm), consisting, according to GLC, of 73% of 1-trifluoromethyl-1,2-dichloroethyl 1'-trifluoromethyl-2'-chloroethyl disulfide (XII) and 27% of 1-trifluoromethyl-2-chlorovinyl 1'-trifluoromethyl-2'-chloroethyl disulfide (XV). The mixture was separated by preparative GLC.

(XII). Found: S 17.82%. $C_6H_5F_6Cl_3S_2$. Calculated: S 17.74%. ^{19}F NMR spectrum: −9.3 d, −9.5 d, and −5.8 s for the CF_3 groups, corresponding to the threo and erythro isomers, intensity ratio 1:1:2, J_{CF_3-CH} = 6.6 Hz. PMR spectrum: 4.2 m (CH, CH_2^1, CH_2^2). Mass spectrum, m/e: 360 M^+, 324 $[M-HCl]^+$, 230 $[CF_3C_2H_2Cl_2S_2H]^+$, 1.96 $[CF_3C_2H_3ClS_2H]^+$, 165 $[CF_3C_2H_2Cl_2]^+$, 157 $[CFC_2H_2Cl_2]^+$, 131 $[CF_3C_2H_3Cl]^+$, 127 $[CF_3C_2H_2S]^+$, 95 $[CF_3C_2H_2]^+$, 69 $[CF_3]^+$, 64 $[S_2]^+$.

(XV). Found: C 22.32; H 1.35; F 34.69; S 19.79%. $C_6H_4F_6Cl_2S_2$. Calculated; C 22.16; H 1.24; F 35.06; S 19.72%. IR spectrum (ν, cm^{-1}): 1590 (C=C). ^{19}F NMR spectrum: −9.1 d (CF_3^1), −14.2 s (CF_3^2); J_{CF_3-CH} = 7.5 Hz. PMR spectrum: 3.9 m (CH, CH_2Cl), 7.4 m (CHCl), intensity ratio 3:1. Mass spectrum, m/e: 324 M^+, 289 $[M-Cl]^+$, 193 $[CF_3C_2HClS_2]^+$, 174 $[CF_2C_2HClS_2]^+$, 161 $[CF_3C_2HClS]^+$, 157 $[CF_3C_2S_2]^+$, 139 $[CF_2C_2HS_2]^+$, 131 $[CF_3C_2H_3Cl]^+$, 107 $[CF_2C_2HS]^+$, 92 $[C_2HClS]^+$, 69 $[CF_3]^+$.

1,1,1-Trifluoro-2,3-dichloropropane-2-sulfenyl Chloride (XVI). a) 32.76 g of bis(1-trifluoromethyl-2-chloroethyl) disulfide (X) [9] and 11 ml of Cl_2 were heated with agitation in a steel autoclave for 12 h at 90°C. After distillation of the reaction mixture a yield of 31 g (66.1%) of (XVI) was obtained, bp 70-73°C (43 mm). Found: C 15.44; H 0.82; F 24.41; S 13.67%. $C_3H_2F_3Cl_3S$. Calculated: C 15.43; H 0.86; F 24.41; S 13.73%. ^{19}F NMR spectrum: −60 s (CF_3). PMR spectrum: 4.7 s (CH_2).

b) 32 g of 1,1,1-trifluoro-3-chloropropane-2-sulfenyl chloride (XI) [9] and 8 ml of Cl_2 was heated with agitation in a steel autoclave for 15 h at 90°C. Distillation gave 32.4 g (86.3%) of (XVI).

Reaction of Sulfenyl Chloride (XVI) with N-Methyl pyrrolidone. N-Methylpyrrolidone (6 ml) was cooled to −40°C and 4.25 g of (XVI) was added dropwise with periodic shaking. The mixture was maintained for 5 days at −10°C, poured into water, and the organic layer was dried over $MgSO_4$ and distilled. Yield 1.84 g of a mixture, bp 80-95°C (1 nm), consisting, according to GLC, of 73.1% of bis(1,trifluoromethyl-1,2-dichloroethyl) disulfide (XVII) and 26.9% of 1-trifluoromethyl-2-chlorovinyl 1'-trifluoromethyl-1',2'-dichloroethyl disulfide (XVIII). A mixture obtained in an analogous manner from three experiments was separated by preparative GLC.

(XVII). Found: C 18.56; H 1.04; S 16.16; F 28.80. $C_6H_4Cl_4F_6S_2$. Calculated; C 18.19; H 1.02; F 28.78; S 16.1%. ^{19}F NMR spectrum: two singlets for the CF_3 groups, corresponding to the threo and erythro isomers, respectively, at −6.4 s and −6.8 s. PMR spectrum: PMR spectrum: 4.4 br. s (CH_2).

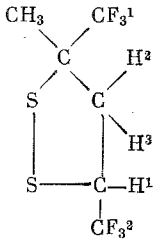
(XVIII). Found: S 17.58%. $C_6H_3F_6Cl_3S_2$. Calculated: S 17.83%. IR spectrum (ν, cm^{-1}): 1590 (C=C). ^{19}F NMR spectrum: −5.1 s (CF_3^1), −15.8 s (CF_3^2). PMR spectrum (in CCl_4): 4.4

m (CH_2Cl), 7.5 m (CHCl), intensity ratio 2:1. Mass spectrum, m/e 358 M^+, 339 $[M - F]^+$, 228 $[CF_3C_2HClS_2Cl]^+$, 193 $[CF_3C_2HClS_2]^+$, 174 $[CF_2C_2HClS_2]^+$, 165 $[CF_3CClCH_2Cl]^+$, 157 $[CF_3C_2S_2]^+$, 139 $[CF_2C_2HS_2]^+$, 129 $[CF_3C_2HCl]^+$, 107 $[CF_2C_2HS]^+$, 92 $[C_2HClS]^+$, 75 $[CF_2C_2H]^+$, 69 $[CF_3]^+$.

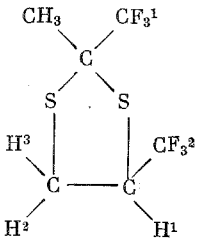
1-Trifluoromethylvinylthiobenzoate (XIX). A mixture of 12.15 g of (XXV) and 20 ml of Et_3N was maintained for 1 day at ∿20°C, and absolute ether was added. Distillation of the filtrate gave 7.2 g (68.6%) of (XIX), bp 95-96°C (2 mm). Found: C 51.73; H 3.01; F 24.62; S 13.68%. $C_{10}C_7OF_3S$. Calculated: C 51.72; H 3.04; F 24.55; S 13.18%.

Reaction of (XIX) with Ammonia. Dry NH_3 was bubbled slowly through 2.68 g of (XIX); the extent of reaction was monitored by GLC. Distillation gave 0.75 g (51%) of a mixture, bp 53-54°C (13 mm), consisting, according to ^{19}F and ^1H NMR spectroscopy, of three isomers (Nos. 1-3) in a 62.7:18.6:18.6 ratio. Isomers: 2,4-bis(trifluoromethyl)-2-methyl-1,3-dithiolane (XXIII) and 3,5-bis(trifluoromethyl)-3-methyl-1,2-dithiolane (XXII), one of which occurs in cis and trans forms. Found: C 28.36; H 2.39; F 44.40; S 24.96%. $C_6H_6F_6S_2$. Calculated: C 28.12; H 2.36; F 44.49; S 25.03%. Mass spectrum, m/e: 256 M^+, 241 $[M - CH_3]^+$ 237 $[M - F]^+$, 187 $[M - CF_3]^+$, 171 $[CF_3C_3H_2S_2]^+$, 153 $[CF_2C_3H_3S_2]^+$, 140 $[CF_2C_2H_2S_2]^+$, 127 $[CF_3C_2H_2S]^+$, 113 $[CF_3CS]^+$, 95 $[CF_3C_2H_2]^+$, 91 $[CH_3CS_2]^+$, 77 $[CS_2H]^+$, 69 $[CF_3]^+$, 64 $[S_2]^+$, 59 $[CH_3CS]^+$, 45 $[CHS]^+$, 15 $[CH_3]^+$.

Isomer No. 1. ^{19}F NMR spectrum: −1.8 s (CF_3^1), −7.1 d (CF_3^2), $J_{CF_3^2-H^1}$ = 10 Hz. PMR spectrum: 1.88 s (CH_3), 3.51 (H^3), 3.68 (H^2), 4.32 q.d.d (H^1), $J_{H^3-H^2}$ = 13.18, $J_{H^3-H^1}$ = 2.5, $J_{H^2-H^1}$ = 6.8, $J_{H^1-CF_3^2}$ = 10 Hz



(XXII)



(XXIII)

Isomer No. 2. ^{19}F NMR spectrum: −3.0 s (CF_3^1), −8.0 d (CF_3^2), $J_{CF_3^2-H^1}$ = 10.0 Hz. PMR spectrum: 1.87 s (CH_3), 3.5 m (H^2, H^3), 4.61 d.q (H^1), $J_{H^1-H^2}$ = 16.5, $J_{H^1-CF_3}$ = 10 Hz.

Isomer No. 3. ^{19}F NMR spectrum: −2.4 br. s (CF_3^1), −9.4 d.q. (CF_3^2), $J_{CF_3^2-H^1}$ = 8.5, $J_{CF_3^1-CF_3^2}$ = 2.5 Hz. PMR spectrum: 1.71 s (CH_3), 2.3 d.d (H^3), 2.96 d.d (H^2), 4.19 m (H^1), $J_{H^2-H^3}$ = 14.5, $J_{H^1-H^2}$ = 7.0, $J_{H^1-CF^3}$ = 8.5 Hz.

1-Trifluoromethyl-2-chloroethylthiobenzoate (XXV). A mixture of 4.8 g 1,1,1-trifluoro-3-chloropropane-2-thiol (XXIV) [9] and 3.36 ml (4.09 g) of benzoyl chloride was heated for 2 days at 140°C and then distilled. Yield 5.14 g (65.9%) of (XXV), bp 114-115°C (1 mm). Found: C 44.83; H 3.08; F 21.15; S 12.13%. $C_{10}H_8OF_3ClS$. Calculated: C 44.70: H 3.00; F 21.21; S 11.93.

1,1,1-Trifluoro-3-chloropropane-2-sulfenamide (XXVIa). A solution of 7 ml dry liquid NH_3 in 50 ml of absolute ether was cooled to −78°C and 14.8 g of 1,1,1-trifluoro-3-chloropropanesulfenyl chloride (XI) [9] was added slowly, dropwise with stirring. Distillation of the filtrate gave 9.35 g (70%) of (XXVIa), bp 55°C (7 mm).

1,1,1-Trifluoro-3-chloropropane-N,N-diethyl-2-sulfenamide (XXVIb). A solution of 16.5 ml of absolute Et_2NH in 85 ml of absolute ether was cooled to −78°C and 15.74 g of (XI) [9] was added slowly, dropwise with stirring. Distillation of the filtrate gave 12.8 (68.7%) of (XXVIb), bp 51-52°C (3 mm). Found: C 35.43; H 5.50; F 24.29; S 13.93%. $C_7H_{13}F_3ClSN$. Calculated: C 35.67; H 5.56; F 24.18; S 13.60%.

CONCLUSIONS

1. Aliphatic, fluorine-containing α,β-unsaturated sulfenamides with terminal double bonds react with dry HCl to give unsymmetrical disulfides.

2. 1,1,1-Trifluoro-3-chloro- and 1,1,1-trifluoro-2,3-dichloropropane-2-sulfenyl chlorides react with N-methylpyrrolidone to give a mixture of fluorine-containing disulfides.

3. The interaction of 1-trifluoromethylvinylthiobenzoate with NH_3 leads to the cyclic dimers of trifluoroacetone: 2,4-bis(trifluoromethyl)-2-methyl-1,3- and 3,5-bis(trifluoromethyl)-3-methyl-1,2-dithiolane.

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REACTION OF 10-VINYLPHENOTHIAZINE WITH BENZOYL PEROXIDE

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The decomposition of benzoyl peroxide (I) by aliphatic and aromatic amines has been the subject of numerous studies [1], whereas the reaction of nitrogenous heterocyclic monomers with (I) has been investigated only in connection with the mechanism of the initiation of the polymerization of 9-vinylcarbazole [2]. We here show that in the case of another highly reactive electron-donor monomer [3] (10-vinylphenothiazine), the reaction of (I) with (II) may follow several pathways:

$$R{-}CH{=}CH_2 + (PhCOO)_2 \rightleftarrows \pi \rightleftarrows [R{-}CH{=}\overset{+}{C}H_2\ (PhCOO)_2^-] \rightarrow$$

$$[R^{\cdot}, \overset{+}{C}H{=}CH_2,\ PhCOO^-,\ PhCOO^{\cdot}].$$

$$RH \xleftarrow[\text{solvent}]{\text{Protic}} R^{\cdot} \xrightarrow[\text{solvent}]{\text{Aprotic}} \begin{cases} \xrightarrow{R^{\cdot}} R{-}R \\ \xrightarrow{PhCOO^{\cdot}} R{-}OOCPh \end{cases}$$

$$PhCOOH \xleftarrow{H^+} PhCOO^- \xrightarrow{\overset{+}{C}H{=}CH_2} PhCOO{-}CH{=}CH_2$$

$$\left[\begin{array}{c} R \\ | \\ -CH-CH_2- \end{array}\right]_n CH{=}CH_2 \xleftarrow{CH_2{=}\overset{+}{C}H} R{-}CH{=}CH_2 \xrightarrow{PhCOO^{\cdot}} PhCOO\left[\begin{array}{c} R \\ | \\ -CH_2-CH- \end{array}\right]_n.$$

The principal end-products obtained from the reaction of equimolar amounts of (I) and (II) were: unsubstituted phenothiazine, 3,10-biphenothiazine, 3-benzoylphenothiazine, benzoic acid, and poly-(10-vinyl-phenothiazine) containing benzoate groups in the chain. Vinyl benzo-

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